A STUDY OF THE VAN DER WAALS FORCE AT SMALL DISTANCES

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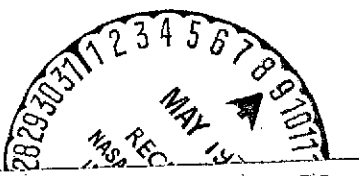

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Abstract

The theory of Dzyaloshinskii allows us to calculate the van der Walls force acting between two surfaces at a distance of 10^4 Å and less from each other. This calculation was based on the experimentally determined absorption data of quartz. The deflection of a thin quartz plate which was supported at one end with a vaporized bar has been measured to verify the theoretical results. Within the range of accuracy a fair agreement could be reached.

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1. Introduction

Up to now, most measurements for determining the van der Waals force were carried out at distances greater than 1000 Å. In this region, the distance dependence of the force can be satisfactorily described by the function B/d^4. For small distances, however, the force acting between two plates as a function of distance varies according to A/d^3. In order to estimate the contribution of the van der Waals force at small distances, familiarity with the transition region of the two distance functions is necessary. For an interpretation of the characteristics of highly dispersed phases, for example,

*Numbers in the margin indicate pagination in the foreign text.

of calcium silicate hydrates, a knowledge of the distance function of the van der Waals force at small distances is of decisive importance. In addition, measurements below 1000 Å allow a more critical examination of the theory.

In an interesting experiment, Tabor and Winterton [1, 2] determined the force between two mica plates down to 50 Å. They succeeded in studying the transition period experimentally for the first time.

Starting from the theory of Dzyaloshinskii [3], we calculated the transition from the B/d^4 law to the A/d^3 law in a previous study [4]. Since the absorption spectrum of quartz was recently measured in a sufficiently large wavelength range, the distance function of the van der Waals force could be calculated by the method described in [4]. These theoretical results will now be checked by experiment. /355

2. Theory

The forces acting between neutral macroscopic bodies can be calculated with the aid of a theory of the van der Waals reciprocal force developed by Dzyaloshinskii et al. [3]. The force between two homogeneous plane-parallel plates at a distance d, for example, is given by

$$F(d)=\frac{\hbar}{2\pi^2c^3}\int_0^\infty d\omega\int_1^\infty dp\,p^2\omega^3\left\{\left[\frac{(s_1+p)(s_2+p)}{(s_1-p)(s_2-p)}\exp\left(\frac{2p\omega d}{c}\right)-1\right]^{-1}+\left[\frac{(s_1+p\varepsilon_1(i\omega))(s_2+p\varepsilon_2(i\omega))}{(s_1-p\varepsilon_1(i\omega))(s_2-p\varepsilon_2(i\omega))}\exp\left(\frac{2p\omega d}{c}\right)-1\right]^{-1}\right\}. \quad (1)$$

where

$$s_{1,2}=\sqrt{\varepsilon_{1,2}(i\omega)-1+p^2}. \quad (2)$$

The dielectric constants of the plates $\varepsilon_1(i\omega)$ and $\varepsilon_2(i\omega)$ are given by

$$\varepsilon_{1,2}(i\omega)=1+\frac{2}{\pi}\int_0^\infty \frac{\omega'\varepsilon''(\omega')\,d\omega'}{\omega^2+\omega'^2}. \tag{3}$$

The temperature function of the van der Waals force is not taken into account in Eq. (1). Thus (1) is valid only for the case

$$\frac{dkT}{\hbar c}\ll 1. \tag{4}$$

At room temperature, the inequality (4) is satisfied up to a distance of 10^4 Å.

In order to calculate the van der Waals force, a knowledge of the absorption spectrum of quartz over a very wide frequency range is required. The necessary measurements have only recently become available [5]. The spectrum used is shown in diagram 1. For the numerical calculation, $\varepsilon''(\omega')$ was replaced by constant values, also shown in the diagram, over small frequency intervals. A better approximation than that given here could of course be made without complications. Yet this does not seem necessary when making comparisons with measured data which are still relatively inaccurate at the present time. In addition, the absorption spectrum is not known precisely enough to justify a more exact calculation. This is particularly true in the infrared region. Two cases are studied in order to investigate the dependence of the van der Waals force on absorption in this frequency range. /356

First, the absorption in the infrared region was completely ignored. The results of the corresponding numerical calculation are given by the dashed line in diagram 2. As expected, Eq. (1) yields an A/d^3 law for small distances ($d \lesssim 5 \cdot 10^{-7}$ cm) and a B/d^4 law for large distances ($d \gtrsim 10^{-5}$ cm).

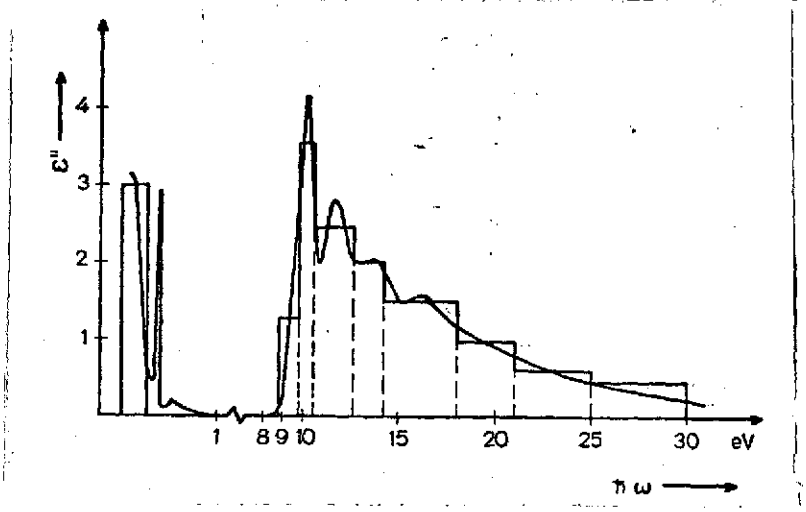

Fig. 1. The experimentally determined absorption spectrum for quartz according to [5]. For the calculation of the van der Waals force, the exact curve was approximated by the step curve which is also sketched in.

The values of A and B are

$$A = 3.46 \cdot 10^{-14} \text{ erg}$$

$$B = 5.87 \cdot 10^{-20} \text{ erg cm}$$

In the intervening region, there is a slow, steady transition between the two distance laws.

In the second case, some simplified assumptions about the course of ε'' in the infrared region were made. In the frequency range $\hbar\omega \approx 0.4$ eV, ε'' undergoes another rapid increase. The exact course of ε'' for smaller frequencies is unknown. Thus ε'' was replaced by the constant value $\varepsilon'' = 3$ in this region, as is shown in the diagram. The extent of this region is determined by the fact that Eq. (3) must yield the static dielectric constant for quartz $\hat{\varepsilon}(0) = 3.7$ for $\omega = 0$. The van der Waals force calculated from this

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spectrum is given by the solid line in Fig. 2. A comparison with the results for the calculation ignoring the infrared contribution shows the following:

The van der Waals constant A for small distances varies only slightly. For large distances and in the transition region, large deviations appear. B is now much larger, and the transition region widens such that a $1/d^4$ law is attained only for $d \gtrsim 10^{-4}$ cm. This places us in a region where temperature corrections must be taken into consideration at room temperature according to inequality (4). The exact values of the van der Waals constants are now: /358

$$A = 3.47 \cdot 10^{-14} \text{ erg}$$

$$B = 1.55 \cdot 10^{-19} \text{ erg cm}$$

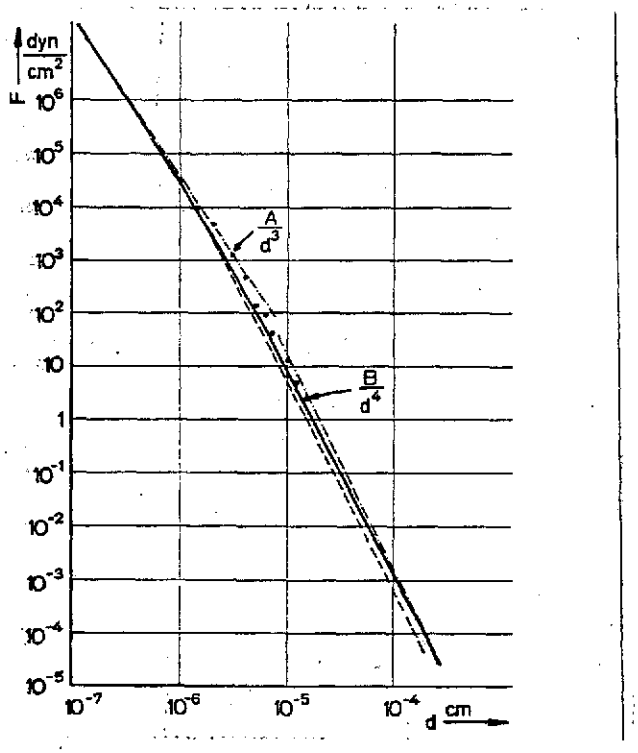

Fig. 2. Distance dependency of the van der Waals force. The calculated function is represented by the solid line. The tangents are represented by the dot-dashed line. The dashed line results from ignoring the infrared portion of the spectrum. The larger dots represent the measured data.

3. Measurements and Results

A new method for measuring the van der Waals forces under 1000 Å was developed. The principle of the method is relatively simple. A small, thin plate, highly polished on both sides, is placed on a thick quartz block whose surface is highly polished. On one end of the small plate, a bar of approximately 1600 Å is evaporated to regulate distance. The force acting between the two bodies causes sag in the small plate, which is in direct contact at the free end. This sag line is measured interferometrically as the inclination of the plate varies. For better resolution, the back of the plate is a reflecting surface. In order to derive the force from the sag line, the following differential equation must be solved:

$$q = E \cdot I \frac{d^4 y}{dx^4} \tag{5}$$

where E = elasticity modulus of the material, I = surface inertial moment with respect to the neutral axis, y = sag, x = local coordinate (extension of the probe) and q = force per unit length.

Since the variation of the sag line is not known in a closed functional expression, but only as a collection of measurement points, the data are evaluated by a computer program which fits the curve to a given series of points using the method of least squares.

The measurements were carried out on quartz glass at a relative humidity in the surrounding atmosphere of approximately 1% and a temperature of 20°C. The evaluation allowed the van der Waals force to be determined in a region from 1600 Å to 80 Å.

The third line in Fig. 2 shows the experimentally determined values of the van der Waals force per unit of surface as a function of distance. Within the limits of measuring accuracy, a good agreement between theory and data is evident. As was already indicated by the measurements of Tabor and Winterton, the unretarded potential slowly transforms into a retarded potential with increasing distance. /359

Material	Authors	Ref.	$B \cdot 10^{20}$ erg cm	$A \cdot 10^{14}$ erg
quartz crystal	Silfhout	6	7.4	
	Hunklinger	7	6.0	
quality glass	Silfhout	6	6.6	
			12.0	
	Black, de Jongh	8	11.5	
			20.0	
	Derjaguin, Abrikosova	9, 10	8.1	
	Geisselmann	11	8.1	
	Kitchener, Prosser	12	11.2	
	Rouweler, Overbeek	13	10.5	
	Our Measurement	—	12.0	3.3
	Calculated Value	—	15.5	3.5

TABLE. COMPARATIVE COMPILATION OF CERTAIN VALUES FOR THE VAN DER WAALS CONSTANT IN THE LITERATURE AND FROM THE RESULTS OF THE PRESENT STUDY.

The table provides a comparison of certain experimentally determined values in the literature with the results of the present study. In the course of our investigations, it became clear that the van der Waals constant is highly dependent on small quantities of adsorbed water. Less than one monolayer is sufficient to reduce the value B in half. A later study will provide more detail in this area. We believe that a reason

for the relatively large variation in the reported van der Waals constants is the fact that very small quantities of adsorbed water cause a reduction of the value which is characteristic for pure quartz surfaces. /360

This study has succeeded in investigating the transition region from retarded to unretarded potential both theoretically and experimentally, facilitating the estimation of the van der Waals force down to very small distances. The contribution of the van der Waals force in adhesion can now be estimated. In addition, it may be possible to correlate the van der Waals force with the surface energy of solid bodies.

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